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(71)Applicant : TORAY IND INC

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(72)Inventor : KOKUNI MASAHIRO

YOKURA MITSUYOSHI

YOSHIMURA TOSHIO

(54) ADHESIVE MATERIAL FOR SEMICONDUCTOR DEVICE, RESIN-LINED METAL FOIL,  
AND WIRING BOARD

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an adhesive material for semiconductor devices wherewith a firm bond is established between a heat-resistant resin film and a metal foil without damaging the physical properties of the heat-resistant resin film and emitting lesser gas during heat treatment, to prepare a resin-lined metal foil, and to provide a wiring board using the resin-lined metal foil.



[I]

SOLUTION: The adhesive material for semiconductor devices has a coating of a polyimide precursor mainly comprising an aromatic tetracarboxylic dianhydride and a diamine on at least one surface of the heat-resistant resin film, wherein the diamine contains a substance represented by formula [I]. In formula [I], R1 is an organic group containing an alkylene group.

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 DN 138:5231  
 ED Entered STN: 27 Nov 2002  
 TI Adhesive films and their use for manufacture of flexible printed circuit boards  
 IN Oguni, Masahiro; Yogura, Mitsuyoshi; Yoshimura, Toshio  
 PA Toray Industries, Inc., Japan  
 SO Jpn. Kokai Tokkyo Koho, 9 pp.  
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 DT Patent  
 LA Japanese  
 IC ICM C09J179-08  
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 H05K001-03; H05K003-38  
 CC 38-3 (Plastics Fabrication and Uses)  
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CLASS

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AB The films are prepared by coating a polyimide precursor derived from aromatic tetracarboxylic dianhydride and an alkylenediamine on a heat-resistant resin film. Preparing a polyimide precursor varnish of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and bis(aminoethyl) ether in AcNMe<sub>2</sub>, coating the varnish on a polyimide film (Upilex S), drying at 80-150° for 35 min, heating 5 min at 250°, electroless plating of a Cu film on the polyimide side, coating with a resist resin, exposing to light with a photomask, and etching gave a printed circuit board with good adhesion.

ST polyimide adhesive film flexible printed circuit board;  
 benzophenonetetracarboxylic dianhydride bisaminoethyl ether polyimide printed circuit boards  
 IT Heat-resistant materials  
 (films, polyimide; adhesive films for manufacture of flexible printed circuit boards)  
 IT Printed circuit boards  
 (flexible; polyimide adhesive films for manufacture of flexible printed circuit boards)  
 IT Polyimides, uses  
 RL: TEM (Technical or engineered material use); USES (Uses)  
 (heat-resistant backing film; polyimide adhesive films for manufacture of flexible printed circuit boards)  
 IT Films  
 (heat-resistant, polyimide; adhesive films for manufacture of flexible

printed circuit boards)

IT Polyimides, uses  
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
 (polyether-; polyimide adhesive films for manufacture of flexible printed circuit boards)

IT Polyketones  
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
 (polyether-polyimide-; polyimide adhesive films for manufacture of flexible printed circuit boards)

IT Polyimides, uses  
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
 (polyether-polyketone-; polyimide adhesive films for manufacture of flexible printed circuit boards)

IT Polyamic acids  
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
 (polyimide adhesive films for manufacture of flexible printed circuit boards)

IT Polyethers, uses  
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
 (polyimide-; polyimide adhesive films for manufacture of flexible printed circuit boards)

IT Polyethers, uses  
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
 (polyimide-polyketone-; polyimide adhesive films for manufacture of flexible printed circuit boards)

IT Adhesive films  
 (polyimide; adhesive films for manufacture of flexible printed circuit boards)

IT 168085-63-0P 476358-86-8P, 3,3',4,4'-Benzophenonetetracarboxylic dianhydride-bis(aminoethyl) ether copolymer 476358-87-9P 476358-88-0P 476614-65-0P  
 RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)  
 (adhesives; polyimide adhesive films for manufacture of flexible printed circuit boards)

IT 9043-05-4 25036-53-7, Kapton EN 25038-81-7 28501-43-1, 1,2,4,5-Benzenetetracarboxylic acid-bis(p-aminophenyl) ether copolymer 29319-22-0 32197-39-0, Upilex S 52685-00-4 71329-95-8 80236-90-4 128280-59-1, Apical NPI  
 RL: TEM (Technical or engineered material use); USES (Uses)  
 (heat-resistant backing film; polyimide adhesive films for manufacture of flexible printed circuit boards)

RN 476358-86-8 REGISTRY

ED Entered STN: 16 Dec 2002

CN 1,3-Isobenzofurandione, 5,5'-carbonylbis-, polymer with  
2,2'-oxybis[ethanamine] (9CI) (CA INDEX NAME)

OTHER NAMES:

CN 3,3',4,4'-Benzophenonetetracarboxylic dianhydride-bis(aminoethyl) ether  
copolymer

MF (C17 H6 O7 . C4 H12 N2 O)x

CI PMS

PCT Polyamic acid, Polyamic acid formed, Polyether, Polyimide, Polyimide  
formed, Polyketone

SR CA

LC STN Files: CA, CAPLUS

\*\*RELATED POLYMERS AVAILABLE WITH POLYLINK\*\*

CM 1

CRN 2752-17-2

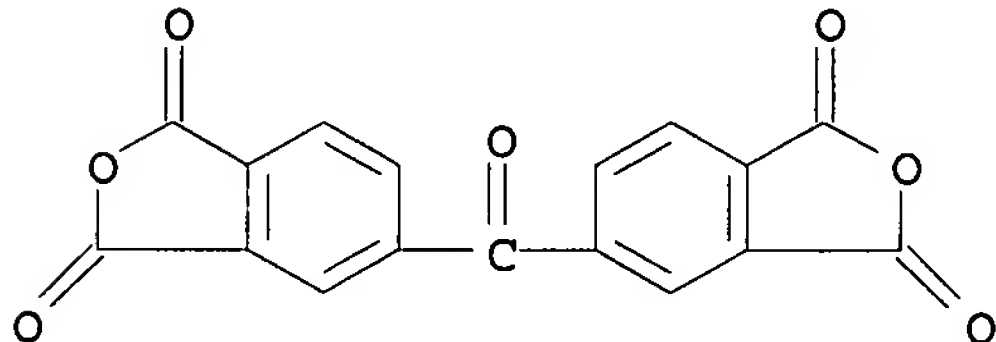
CMF C4 H12 N2 O

H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>

CM 2

CRN 2421-28-5

CMF C17 H6 O7



1 REFERENCES IN FILE CA (1907 TO DATE)

1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

DERWENT-ACC-NO: 2003-304419

DERWENT-WEEK: 200350

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TITLE: Adhesive materials for semiconductor devices obtained by applying polyimide precursor consisting mainly of aromatic tetracarboxylic dianhydride and diamine to at least one side of heatresistant resin film

PATENT-ASSIGNEE: TORAY IND INC[TORA]

PRIORITY-DATA: 2001JP-0152406 (May 22, 2001)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAINIPC
<u>JP 2002338929 A</u>	November 27, 2002	N/A	009	C09J 179/08

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2002338929A	N/A	2001JP-0152406	May 22, 2001

INT-CL (IPC): B32B015/08, C08G073/10 , C08L079/08 , C09J007/02 , C09J179/08 , H01L021/60 , H05K001/03 , H05K003/38

ABSTRACTED-PUB-NO: JP2002338929A

BASIC-ABSTRACT:

NOVELTY - Adhesive materials for semiconductor devices are obtained by applying a polyimide precursor, consisting mainly of an aromatic tetracarboxylic dianhydride and a diamine containing a compound (I), to at least one side of a heat-resistant resin film.

DETAILED DESCRIPTION - Adhesive materials for semiconductor devices are obtained by applying a polyimide precursor, consisting mainly of an aromatic tetracarboxylic dianhydride and a diamine containing a compound (I), to at least one side of a heat-resistant resin film

NH2-R1-NH2 (I)

R1 = organic group containing an alkylene group.

INDEPENDENT CLAIMS are also included for the following:

(1) metal foils with a resin obtained by laminating a metal layer onto the adhesive materials; and

(2) wired boards made using the metal foils.

USE - The adhesive materials for semiconductor devices are useful for metal foils with a resin and the metal foils are suitable for flexible wiring boards.

ADVANTAGE - The adhesive materials can maintain physical properties characteristic of heat-resistant resin films, generate little gas on heating and can adhere a heat-resistant resin film and a metal foil strongly.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: ADHESIVE MATERIAL SEMICONDUCTOR DEVICE OBTAIN APPLY POLYIMIDE  
PRECURSOR CONSIST MAINLY AROMATIC ONE SIDE HEAT RESISTANCE RESIN  
FILM

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the charge for semiconductor devices of a binder, the metallic foil with resin, and patchboard which are used for manufacture of a flexible patchboard.

[0002]

[Description of the Prior Art] From the former, a heat-resistant-resin film employs the description peculiar to the resin efficiently, and is used in various fields. For example, FPC (flexible printed circuit board), a tape carrier package tape for TAB (tape automated bonding), etc. which carried out the laminating with a metallic foil and adhesives are well known. These stick a heat-resistant-resin film and metallic foils, such as polyimide, using adhesives, such as an epoxy resin system, an acrylic resin system, a polyamide resin system, and an NBR (acrylonitrile-butadiene rubber) system. Such many properties of FPC or a tape carrier package tape are influenced by the engine performance of the adhesives to be used in the present condition, and the outstanding thermal resistance or the other outstanding properties which a heat-resistant-resin film has are not fully employed efficiently. For this reason, although the thermal resistance of polyimide is 350 degrees C or more even if it uses a polyimide film, the solder thermal resistance of FPC or a tape carrier package tape will usually become 300 degrees C or less.

[0003] Furthermore, a metallic foil is not stuck but how to form a thin metal layer for a metal according to wet process on a spatter or adhesives, and form a metal layer further by plating after that on adhesives, such as an epoxy resin system, an acrylic resin system, a polyamide resin system, and an NBR system, is also learned.

[0004]

[Problem(s) to be Solved by the Invention] After applying a polyimide precursor thru/or the organic polar-solvent solution of polyimide to a metallic foil front face directly as an approach of solving such a trouble, without using adhesives, desiccation removal of a solvent and the approach of imide-izing are also learned. However, in order not to use adhesives, when the adhesive properties of a metallic foil and polyimide ran short, patterning of the metal layer was carried out and wiring was formed, there was a problem on which a wiring layer exfoliates from polyimide.

[0005]

[Means for Solving the Problem] That is, it is the charge for semiconductor devices of a binder which this invention is the charge of a binder which applied at least to one side of a heat-resistant-resin film the polyimide precursor which uses aromatic series tetracarboxylic dianhydride and diamine as a principal component, and is characterized by including that diamine is indicated to be by the general formula [I].

[0006]

[Formula 2]



[0007] (R1 shows the organic radical containing an alkylene group among a formula.)



[0008]

[Embodiment of the Invention] The charge for semiconductor devices of this invention of a binder applies the polyimide precursor which used as the principal component beforehand diamine which has aromatic series tetracarboxylic dianhydride and a flexible frame as an adhesives layer on the heat-resistant-resin film used as a base film, and the metallic foil with resin of this invention forms a metal layer on this charge of a binder.

[0009] As a heat-resistant-resin film used as a base film Polyarylate, polysulfone which are the condensate of the dicarboxylic acid of bisphenols, Or the condensate of the poly allyl compound sulfone, benzotetracarboxylic acid, and aromatic series isocyanate which are represented by polyether sulphone, Or bisphenols, aromatic series diamine, thermosetting polyimide obtained from the reaction of a nitro phthalic acid, Although what used resin, such as aromatic polyimide, aromatic polyamide, an aromatic series polyether amide, polyphenylene SURUFADO, the poly allyl compound ether ketone, polyamidoimide, and a liquid crystal polymer, as the film is mentioned, it is not limited to these. As a concrete product, "Kapton" by Du Pont-Toray, "YUPI REXX" by Ube Industries, Ltd., "APIKARU" by Kaneka Co., Ltd., "MIKUTORON" by Toray Industries, Inc., and "BEKITORA" By Kuraray etc. are mentioned.

[0010] These trees In these resin, the aromatic polyimide which is the condensate of aromatic polyimide, aromatic polyamide especially pyromellitic acid 2 anhydride or biphenyl tetracarboxylic dianhydride, and aromatic series diamines, such as diamino diphenyl ether and a p phenylenediamine, is desirable.

[0011] The above-mentioned thermal resistance It is desirable to perform plasma treatment arbitrary [ performing corona discharge treatment, low-temperature plasma treatment or well-known wet process processing, etc. to the above-mentioned heat-resistant-resin film front face ] and especially suitable in respect of the improvement in adhesive strength.

[0012] As thickness of a heat-resistant-resin film, 5-125 micrometers is 20-80 micrometers more preferably. Since trouble will be caused to the conveyance nature of a film if too thin, the above-mentioned range is desirable.

[0013] The polyimide precursor applied at least to one side of the above-mentioned heat-resistant-resin film functions as adhesives on which the heat-resistant-resin film which is a base film, and a metal layer are pasted up. Such a polyimide precursor uses as a principal component aromatic series tetracarboxylic dianhydride and diamine which has a flexible frame.

[0014] As an example of aromatic series tetracarboxylic dianhydride Pyromellitic acid 2 anhydride, 3, 3', 4, 4'-biphenyl tetracarboxylic dianhydride, 2, 3, 3', - biphenyl tetracarboxylic dianhydride, 3, 3', and 4 '4, 4'-benzophenone tetracarboxylic dianhydride, - benzophenone tetracarboxylic dianhydride, 2, 2', and 2, 2', 3, and 3 '3, 3'-biphenyl tetracarboxylic dianhydride, 2 and 2-bis(3, 4-dicarboxy phenyl) propane 2 anhydride, 2 and 2-bis(2, 3-dicarboxy phenyl) propane 2 anhydride, Bis(3, 4-dicarboxy phenyl) ether 2 anhydride, bis(3, 4-dicarboxy phenyl) sulfone 2 anhydride, 1 and 1-bis(2, 3-dicarboxy phenyl) ethane 2 anhydride, bis(2, 3-dicarboxy phenyl) methane 2 anhydride, 2, 3, 6, 7-naphthalene tetracarboxylic dianhydride, 1, 4 and 5, 8-naphthalene tetracarboxylic dianhydride, 1, 2, 5, 6-naphthalene tetracarboxylic acid, 1, 2 and 3, 4-benzene tetracarboxylic dianhydride, 3, 4, 9, 10-perylene tetracarboxylic dianhydride, 2, 3 and 6, 7-anthracene tetracarboxylic dianhydride, 1, 2 and 7, 8-phenanthrene tetracarboxylic dianhydride, etc. are mentioned. these acid 2 anhydrides -- one sort -- or two or more kinds are mixed and it is used.

[0015] As diamine preferably used by this invention, what is expressed with a general formula [I] is mentioned preferably.

[0016]

[Formula 3]



[0017] R1 shows the organic radical containing an alkylene group among a formula. As an alkylene group, a methylene group, ethylene, a propylene radical, a butylene radical, a hexylene radical, an octylene radical, a polymethylene radical, etc. are mentioned, and these may have the suitable

substituent and may include ether linkage, an ester bond, amino association, amide association, a urethane bond, urea association, carbonate association, etc. in the chain in the chain. Although an alkyl group, a phenyl group, a methoxy group, a phenoxy group, a nitro group, a hydroxyl group, the amino group, a fluorine atom, a chlorine atom, etc. are mentioned as a substituent in this case, it is not limited to these. Although two or more sorts are mixed and it is used, as for the diamine which has such a flexible frame, it is desirable independent or for two or more sorts to be mixed and to use from the purpose for which demand characteristics, such as an adhesive property and thermal resistance, are satisfied.

[0018] Moreover, it is desirable from the point that mixing the diamine except being shown by the general formula [I] if needed also pulls out both [ heat-resistant ] the function as adhesives, and polyimide. Although not limited especially as such diamine, 4 and 4'-diamino diphenyl ether, - diamino diphenylmethane, and 4 and 4' 4, 4'-diaminodiphenyl sulfone, A p phenylenediamine, 1, 1 and 3, 3-tetramethyl - 1, 3-bis(4-aminophenyl) disiloxane, The 1, 1, 3, and 3-tetra-phenoxy -1, 3-bis(2-aminoethyl) disiloxane, 1, 1, 3, 3, 5, and 5-hexa methyl -1, 5-bis(4-aminophenyl) trisiloxane, The 1, 1, 3, and 3-tetra-phenyl -1, 3-bis(2-aminoethyl) disiloxane, The 1, 1, 3, and 3-tetra-phenyl -1, 3-bis(3-aminopropyl) disiloxane, The 1, 1, 5, and 5-tetra-phenyl -3, the 3-dimethyl -1, 5-bis(3-aminopropyl) trisiloxane, The 1, 1, 5, and 5-tetra-phenyl -3, 3-dimethoxy -1, 5-bis(4-aminopropyl) trisiloxane, The 1, 1, 5, and 5-tetra-phenyl -3, 3-dimethoxy -1, 5-bis(5-amino pentyl) trisiloxane, 1, 1, 3, and 3-tetramethyl - 1, 3-bis(2-aminoethyl) disiloxane, 1, 1, 3, and 3-tetramethyl - 1, 3-bis(3-aminopropyl) disiloxane, 1, 1, 3, and 3-tetramethyl - 1, 3-bis(4-amino butyl) disiloxane, 1, the 3-dimethyl -1, 3-dimethoxy -1, 3-bis(4-amino butyl) disiloxane, 1, 1, 5, and 5-tetramethyl - 3 and 3-dimethoxy -1, 5-bis(2-aminoethyl) trisiloxane, 1, 1, 5, and 5-tetramethyl - 3 and 3-dimethoxy -1, 5-bis(4-amino butyl) trisiloxane, 1, 1, 5, and 5-tetramethyl - 3 and 3-dimethoxy -1, 5-bis(5-amino pentyl) trisiloxane, Although 1, 1, 3, 3, 5, and 5-hexa methyl -1, 5-bis(3-aminopropyl) trisiloxane, 1, 1, 3, 3 and 5, 5-hexa propyl -1, 5-bis(3-aminopropyl) trisiloxane, etc. are mentioned It is not limited to these but ether linkage, an ester bond, amino association, amide association, a urethane bond, urea association, carbonate association, etc. may be included in the chain. such diamines are independent -- or two or more sorts can be mixed and it can use.

[0019] As for the rate of the diamine which corresponds to a general formula [I] to all diamine compounds, in the polyimide precursor of this invention, it is desirable from the point of the curl prevention effectiveness after imide-izing, and the adhesive improvement effectiveness that it is more than 50mol%.

[0020] The reaction of the above-mentioned aromatic series tetracarboxylic dianhydride and diamine should just make aromatic series tetracarboxylic acid, or its anhydride and diamine of the amount of abbreviation stoichiometries react at 0-80 degrees C in organic solvents, such as N.N-dimethylformamide, N,N-dimethylacetamide, and a N-methyl-2-pyrrolidone. Two or more sorts are mixed and it is used, and as long as it is that these organic solvents are independent or extent in which a polyimide precursor does not deposit, solvents, such as benzene, toluene, a hexane, a cyclohexane, a tetrahydrofuran, and a methyl ethyl ketone, may be added. Although especially polyimide precursor varnish concentration is not limited, 5 - 60 % of the weight is desirable, and especially 10 - 40 % of the weight is desirable.

[0021] In the charge for semiconductor devices of a binder and the metallic foil with resin of this invention, the polyimide precursor is applied on a heat-resistant-resin film. In order to pull out the engine performance as polyimide about imide-izing of a polyimide precursor, it is desirable to be carried out before the metal stratification, and it is desirable to be carried out immediately after applying a polyimide precursor to a heat-resistant-resin film especially. Since the polyimide precursor used in this invention is thermoplasticity after imide-izing it, it has the advantage which can be used as adhesives in the state of polyimide. Since water is generated in the case of hardening, i.e., imide-izing, in the case of thermosetting polyimide, this water will become gas and foaming will arise.

[0022] Although foaming of the polyimide precursor [ after imide-izing in this invention ] by the gas of water and others decreases since there is little generating gas at the time of heat-treatment, it is desirable



that the capacity generated in 100-300 degrees C whenever [ stoving temperature / after imide-izing ] is 250 ppm or less. 150 ppm or less are 100 ppm or less still more preferably more preferably. With the capacity generated in 100-300 degrees C here whenever [ stoving temperature ], it measures according to thermogravimetric analysis, differential solution gravimetric analysis, and a mass spectrometry, and asks.

[0023] Next, the manufacture approach of the charge for semiconductor devices of above-mentioned this invention of a binder is explained.

[0024] First, the solvent solution containing the above-mentioned polyimide precursor varnish is made to breathe out from the slit for film production on a heat-resistant-resin film, and it applies to homogeneity. As the method of application, what is depended on a roll coater, a knife coating machine, a seal coating machine, a comma coating machine, a doctor blade float coating machine, etc. is mentioned. Next, after carrying out heating removal of the solvent of the solution applied to the heat-resistant-resin film as mentioned above in 1 - 60 minutes continuously [ in the temperature of about 60-190 degrees C ], or intermittently, heat-treatment for making imide-izing and the amount of generation of gas with 250 ppm or less further is performed. As heat-treatment for making imide-izing and the amount of generation of gas with 250 ppm or less, it is desirable to perform heat-treatment for about 1 - 15 minutes in 200-350 degrees C. Thus, a polyimide precursor is imide-ized, the polyimide film is formed, and the charge for semiconductor devices of a binder is obtained.

[0025] Moreover, it is desirable that the elastic modulus after imide-izing of a polyimide precursor becomes smaller than the elastic modulus of a heat-resistant-resin film in this invention.

[0026] As thickness after imide-izing a polyimide precursor, 0.05-50 micrometers is 0.1-25 micrometers more preferably. The adhesion effectiveness will become weak if too thin.

[0027] In this invention, it is also desirable to have a catalyst nucleus in a polyimide precursor. Although it does not work as a nucleus of plating growth if the catalyst nucleus said here remains as it is, it works as a nucleus of plating growth by carrying out activation. Although usually added by the condition of a polyimide precursor varnish, depending on the case, you may add after heat-resistant-resin film spreading, and after addition of a catalyst nucleus imide-izes a polyimide precursor, it may be added. A catalyst nucleus serves as a core at the time of forming a metal layer by plating, palladium, its nickel, chromium, etc. are desirable, and its palladium is still more desirable. The content rate of the catalyst nucleus contained in the above-mentioned polyimide precursor is the 0.001 - 100 weight section to the polyimide precursor 100 weight section preferably.

[0028] Next, in the case of a metallic foil with resin, a metal layer is formed on the film which imide-ized the polyimide precursor or the precursor. As the metal stratification approach, the approach of sticking a metallic foil, the approach by the spatter or vacuum evaporation, the approach by plating, etc. are mentioned. As a metal which constitutes a metal layer, although copper, nickel, chromium, tin, zinc, lead, gold, a rhodium, palladium, etc. are mentioned, it is not limited to these. These metals may be used independently, or more than one may be combined and they may be used.

[0029] When sticking a metallic foil, it is desirable to paste up a metallic foil by processing at hot 100-350 degrees C at 70-350 degrees C, a lamination or after laminating at 40-200 degrees C of low temperature comparatively.

[0030] In a spatter or vacuum evaporation, a metal layer is formed on adhesives so that it may become suitable thickness, for example, the thickness of 0.0001-10 micrometers.

[0031] In plating, it is common to form the metal thin film which does not perform direct plating but serves as a nucleus before plating on the film which imide-ized the polyimide precursor or the precursor, and to plate it after an appropriate time. It is divided into wet process and a dry process as an approach of forming the metal thin film used as such a nucleus. In the case of wet process, it is divided by the case where it does not have with the case where the film which imide-ized the polyimide precursor or the precursor further has the catalyst nucleus. When it does not have the catalyst nucleus, first, palladium, nickel, chromium, etc. process catalyst grant, and if required, the given catalyst will be activated. A catalyst will be activated, if required when it has the catalyst nucleus. In the case of a dry process, the spatter of the metals, such as chromium, and nickel, copper, is carried out to the film which imide-ized

the polyimide precursor or the precursor, but the spatter of the metals, such as copper, may be carried out independently, and a spatter may be carried out combining chromium-copper, nickel-copper, etc. Although especially the thickness of the metal thin film used as a nucleus is not specified, it is 1-1000nm preferably. If too thick, metal thin film formation will take time amount, and if too thin, a fault will become plating produced and mentioned later with a failure. Thus, a metal layer is formed by plating on the formed metal thin film. Although a metal layer may be formed only by electroless deposition, it may use together and form electroless deposition and electrolytic plating, and may form them only by electrolytic plating. When plating copper as electroless deposition, the combination of a copper sulfate and formaldehyde etc. is used. Moreover, when plating copper as electrolytic plating, copper-sulfate plating liquid, copper-cyanide plating liquid, copper pyrophosphate plating liquid, etc. are usually used.

[0032] A metal bed depth is influenced by how a metallic foil with resin is processed. That is, since the laminating of the metal is further carried out by plating on a metal layer when forming a patchboard by the additive method (a semi additive method or full additive method) using a metallic foil with resin, the metal bed depth of a metallic foil with resin has the desirable range of 0.1-10 micrometers. Conversely, since a metallic foil is used as wiring as it is when forming a patchboard by the subtractive method using a metallic foil with resin, the metal bed depth of a metallic foil with resin has the desirable range of 3-40 micrometers.

[0033] As a series of strokes which form the above-mentioned metal layer, the following procedures are mentioned, for example. That is, counter etching of the adhesive coated surface of the charge for semiconductor devices of a binder which imide-ized the polyimide precursor or precursor first applied to the heat-resistant-resin film, and surface washing are performed. Next, software etching is carried out, a sulfuric acid performs acid cleaning, and pretreatment by the hydrochloric acid is performed. Catalytic activity-ized processing is performed after performing catalytic activity-ized processing succeedingly when the catalyst nucleus contains, and performing catalyst grant, when the catalyst nucleus does not contain. Non-electrolyzed metal plating is performed to after an appropriate time, if required, electrolysis metal plating will be performed after electroless deposition, and a metal layer will be formed.

[0034] In this invention, the charge for semiconductor devices of a binder was produced by forming the film which imide-ized the polyimide precursor or precursor which can serve as adhesives on the heat-resistant-resin film used as a base film, the metal layer was formed on it, and the metallic foil with resin has been obtained. By imide-izing a polyimide precursor, also when firm adhesive strength is obtained and a metal layer is especially etched into a predetermined circuit pattern rather than it forms a direct metal layer on a heat-resistant-resin film, good adhesive strength can be obtained.

[0035] Setting to this invention, adhesive strength is JIS. C5016 Although a pattern with a conductor width of 3mm is used, the value when tearing off a metallic foil the rate for 50mm/in the direction of 180 degrees is meant according to the 7.1st term, and 5 or more N/cm is desirable and is usually more preferably made into 10 or more N/cm, according to the metallic foil with resin of this invention, it becomes possible to acquire the value of 10 or more N/cm easily. Moreover, it also has the advantage to which a heat-resistant-resin film does not spoil the property which it originally has.

[0036] The metallic foil with resin of above-mentioned this invention etches a metal layer at the configuration which suited the circuit pattern by forming a resist layer on a metal layer, and exposing and developing a resist layer by using as an etching mask the resist which carried out patterning of the resist and carried out patterning, forms a circuit pattern, and is preferably used as a patchboard obtained by removing a resist after circuit pattern formation.

[0037] Moreover, as for the metallic foil with resin of above-mentioned this invention, it is also desirable to consider as the patchboard obtained by forming a circuit pattern in the part which removed the resist of the part which forms a resist layer on a metal layer and forms a circuit pattern by exposing and developing a resist layer, and removed the resist by plating, exfoliating a resist after that, and removing metal layers other than a circuit pattern.

[0038] The metallic foil with resin of this invention has the metal layer to one side or both sides of a

heat-resistant-resin film, by forming wiring using a semi additive method or a subtractive method, can form one side or a double-sided patchboard, and can use it for a flexible patchboard application preferably.

[0039]

[Example] This invention is not limited by these examples, although an example is given below and this invention is explained.

[0040] the diamines 10.4g (0.1 mols) and 3 which permuted the inside of the 500ml flask equipped with synthetic example 1 thermometer, churning equipment, and a dephlegmator by the bottom of nitrogen-gas-atmosphere mind, put in 128.8g of N,N-dimethylacetamide, and were shown below, 3', and 4 and 4 - - ' -- 32.2g (0.1 mols) of - benzophenone tetracarboxylic dianhydride was added, under nitrogen-gas-atmosphere mind, it was made to react, agitating at 50 degrees C succeedingly by 10 degrees C for 3 hours for 1 hour, and the polyimide precursor varnish be obtained.

[0041]

[Formula 4]



[0042] 5g of palladium catalyst nuclei was added on the polyimide precursor varnish obtained in the example 1 of synthetic example 2 composition, and the catalyst nucleus content polyimide precursor varnish was obtained.

[0043] 166.8g of N,N-dimethylacetamide is put in using the same reaction container as the example 1 of synthetic example 3 composition. Diamine 7.4g (0.05 mols) shown below, ethylenediamine 0.6g (0.01 mols), P phenylenediamines 4.3g (0.04 mols) and 3, 3', and 4 and 29.4g (0.10 mols) of 4'-biphenyl tetracarboxylic dianhydride are added. Under nitrogen-gas-atmosphere mind, it was made to react, agitating at 50 degrees C succeedingly by 10 degrees C for 3 hours for 1 hour, and the polyimide precursor varnish was obtained.

[0044]

[Formula 5]

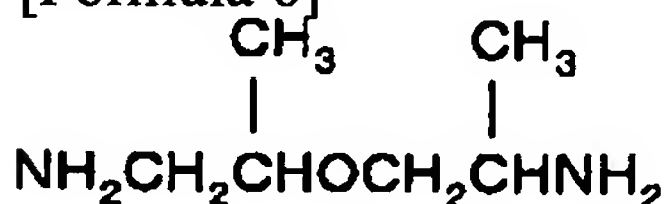


[0045] 3g of palladium catalyst nuclei was added on the polyimide precursor varnish obtained in the example 2 of synthetic example 4 composition, and the catalyst nucleus content polyimide precursor varnish was obtained.

[0046] 191.2g of N,N-dimethylacetamide is put in using the same reaction container as the example 1 of synthetic example 5 composition. Diamine 6.6g (0.05 mols) shown below, hexamethylenediamine 1.2g (0.01 mols), 1, 1, 3, and 3-tetramethyl - 1, 3-bis(aminomethyl) disiloxane 1.9g (0.01 mols), 4 and 4'-diamino diphenylmethane 5.9g (0.03 mols), 3, 3', and 4 and 32.2g (0.1 mols) of 4'-benzophenone tetracarboxylic dianhydride were added, under nitrogen-gas-atmosphere mind, it was made to react, agitating at 50 degrees C succeedingly by 10 degrees C for 3 hours for 1 hour, and the polyimide precursor varnish was obtained.

[0047]

[Formula 6]



[0048] 10g of palladium catalyst nuclei was added on the polyimide precursor varnish obtained in the example 5 of synthetic example 6 composition, and the catalyst nucleus content polyimide precursor varnish was obtained.

[0049] Using the same reaction container as the example 1 of synthetic example 7 composition, 172g of N,N-dimethylacetamide was put in, p phenylenediamine 10.8g was dissolved, and 3, 3', and the polyimide precursor varnish that is made to react, agitating at 50 degrees C succeedingly by 10 degrees



C under nitrogen-gas-atmosphere mind by adding 4 and 32.2g of 4'-benzophenone tetracarboxylic dianhydride for 3 hours for 1 hour, and does not contain siloxane system diamine were obtained.

[0050] It applied so that the thickness after drying the polyimide precursor varnish compounded in the synthetic example 1 on one side of the polyimide film "YUPI REXX S" by Ube Industries, Ltd. of 150 micrometer thickness of examples might be set to 12 micrometers, and it dried for 10 minutes at 80 degrees C first, then, dried for 10 minutes at 130 degrees C, and dried for 15 minutes at 150 more degrees C. Subsequently, heating was performed at 250 degrees C for 5 minutes as processing which controls imide-izing and generating capacity.

[0051] Next, the side which imide-ized the polyimide precursor of the obtained charge of a binder is degreased by isopropanol. Carry out software etching with a sodium-hydroxide content solution, and a hydrochloric acid neutralizes. Catalyst grant is carried out in Okuno Drug industry OPC-50 inducer. Reduction processing was performed in Okuno Drug industry OPC-150 cristae, it plated with non-electrolytic copper plating to 0.5 micrometers in thickness after that, finally the copper layer with a thickness of 35 micrometers was formed by electrolytic copper plating, and the metallic foil with one side resin whose metal layer is copper was obtained.

[0052] When 250 degrees C was heat-treated for 1 hour and the amount of generation of gas was measured after the metallic foil formation with resin, it is 42 ppm and peeling of the metal layer by the generation of gas etc. was not observed. Moreover, it is JIS in order to investigate the adhesive strength of the metal layer and base material film in the formed metallic foil with resin. C5016 It was 12 N/cm when the value when using a pattern with a conductor width of 3mm and tearing off a metal layer the rate for 50mm/in the direction of 180 degrees according to the 7.1st term was measured.

[0053] On the metal layer of the metallic foil with resin of obtained one side, the photoresist was applied and dried so that desiccation thickness might be set to 5 micrometers, exposure and development were given using the mask suitable for a circuit pattern [ as / whose line breadth is 5-100 micrometers ], and the resist pattern with which only the wiring layer pattern part remained was obtained. Next, the metal of a part from which the resist was removed was etched in the ferric chloride water solution 10%, and the one side patchboard was obtained. In the obtained patchboard, thin wiring of 5-micrometer width of face had also pasted up firmly comparatively thick wiring of 100-micrometer width of face with the film, and lack of a circuit pattern etc. was not seen.

[0054] In example of comparison 1 example 1, the metallic foil with resin was produced like the example 1 except having used the varnish compounded in the synthetic example 7 instead of the polyimide precursor varnish compounded in the synthetic example 1. The amount of generation of gas is 1350 ppm, and peeling of a metal layer produced it in the a large number part. When the adhesive strength of a metal layer and a base material film was measured like the example 1, it was 1 or less N/cm, and the metal layer and the base material film exfoliated simply, and it was not practical use level.

[0055] The polyimide precursor varnish compounded in the synthetic example 2 instead of the polyimide precursor varnish compounded in the example 1 of example 2 composition was used, and processing which controls spreading, desiccation, imide-izing, and generating capacity like an example 1 was performed.

[0056] The side which imide-ized the polyimide precursor varnish of the obtained charge for semiconductor devices of a binder is degreased by isopropanol. Carry out software etching with a sodium-hydroxide content solution, and a hydrochloric acid neutralizes. Reduction processing is performed in Okuno Drug industry OPC-150 cristae. Electroless nickel plating was given in Okuno Drug industry TMP chemistry nickel HR-T, it plated with non-electrolytic copper plating to 1 micrometer in thickness after that, finally the copper layer with a thickness of 3 micrometers was formed by electrolytic copper plating, and the metallic foil with one side resin whose metal layer is copper was obtained.

[0057] After the metallic foil formation with resin, when the amount of generation of gas was measured, it is 42 ppm and peeling of the metal layer by the generation of gas etc. was not observed. Moreover, it was 13 N/cm when the value when tearing off like an example 1 was measured, in order to investigate



the adhesive strength of the metal layer and base material film in the formed metallic foil with resin.

[0058] On the metal layer of the metallic foil with resin of obtained one side, the photoresist was applied and dried so that desiccation thickness might be set to 5 micrometers, exposure and development were given using the mask suitable for a circuit pattern [ as / whose line breadth is 5-100 micrometers ], and the resist pattern from which only the wiring layer pattern part was removed was obtained. Next, non-electrolytic copper plating and electrolytic copper plating were performed to the metal of a part from which the resist was removed, and it plated to 4.5 micrometers. Tinning and gold plate were performed after that and it plated to 5 micrometers which is finally the same height as a resist. The resist was removed after plating termination, subsequently software etching was carried out using the ferric chloride water solution, metals other than a wiring part were removed, and the one side patchboard was obtained. In the obtained patchboard, thin wiring of 5-micrometer width of face had also pasted up firmly comparatively thick wiring of 100-micrometer width of face with the film, and lack of a circuit pattern etc. was not seen.

[0059] Plasma treatment was first performed on both sides of the Du Pont-Toray polyimide film "Kapton EN" of 350 micrometer thickness of examples, it applied so that the thickness after drying the polyimide precursor varnish compounded in the synthetic example 3 might be set to 18 micrometers, and it dried for 10 minutes at 80 degrees C first, then, dried for 10 minutes at 120 degrees C, and dried for 15 minutes at 150 more degrees C. Subsequently, heat-treatment was performed to this spreading article at 210 degrees C for 5 minutes, and processing which controls imide-izing and generating capacity was performed.

[0060] It washes by cleaner conditioner DP-110. after [ thus, ] imide-izing the polyimide precursor of the obtained charge for semiconductor devices of a binder -- the product made from Ebara YUJI Light -- Software etching is carried out using DP-200 and a sulfuric acid. the product made from Ebara YUJI Light -- It dips pre using DP-300 and a hydrochloric acid. the product made from Ebara YUJI Light -- Catalyst grant is carried out using DP-300, DP-350, and a hydrochloric acid. the product made from Ebara YUJI Light -- A catalyst is activated using DP-400 A-D made from Ebara YUJI Light, and DP-410. Reduction processing of a catalyst is performed using DP-500. the product made from Ebara YUJI Light -- Acid cleaning was performed in PB-242D made from Ebara YUJI Light, acid cleaning was carried out with the sulfuric acid, electrolytic copper plating was performed using the copper sulfate after that, the copper layer with a thickness of 8 micrometers was formed in both sides, and the metallic foil with resin whose double-sided metal layer is copper was obtained.

[0061] After the metallic foil formation with resin, when the amount of generation of gas was measured, it is 45 ppm and peeling of the metal layer by the generation of gas etc. was not observed. Moreover, it was 14 N/cm when the value when tearing off a metal layer like an example 1 was measured.

[0062] The resist pattern was produced using the example 1, the same resist, and the mask on the metal layer of both sides of the obtained metallic foil with resin, the double-sided metal was etched like the example 1, the double-sided resist was removed, and the double-sided patchboard was obtained. In the obtained patchboard, both sides had also pasted up firmly comparatively thick wiring of 100-micrometer width of face also for thin wiring of 5-micrometer width of face with the film, and lack of a circuit pattern etc. was not seen.

[0063] The polyimide precursor varnish compounded in the synthetic example 4 instead of the polyimide precursor varnish compounded in the example 3 of example 4 composition was used, and the pre DIP process made it be the same as that of an example 3. Next, a catalyst is activated using DP-400 A-D made from Ebara YUJI Light, and DP-410. Reduction processing of a catalyst is performed using DP-500. the product made from Ebara YUJI Light -- Acid cleaning was performed in PB-242D made from Ebara YUJI Light, acid cleaning was carried out with the sulfuric acid, electrolytic copper plating was performed using the copper sulfate after that, the copper layer with a thickness of 2 micrometers was formed in both sides, and the metallic foil with resin whose double-sided metal layer is copper was obtained.

[0064] After the metallic foil formation with resin, when the amount of generation of gas was measured, it is 45 ppm and peeling of the metal layer by the generation of gas etc. was not observed. Moreover, it

was 15 N/cm when the value when tearing off a metal layer like an example 1 was measured.

[0065] The resist pattern with a thickness of 15 micrometers was produced using the example 2, the same resist, and the mask on the metal layer of both sides of the obtained metallic foil with resin, and electrolytic copper plating was performed and it plated to 15 micrometers in thickness which is the same height as a resist. The resist was removed after that, subsequently software etching of the whole was carried out using the copper chloride water solution, and the double-sided patchboard was obtained by removing metals other than a wiring part. In the obtained patchboard, thin wiring of 5-micrometer width of face had also pasted up firmly comparatively thick wiring of 100-micrometer width of face with the film, and lack of a circuit pattern etc. was not seen.

[0066] Plasma treatment was first performed on both sides of the polyimide film "APIKARU NPI" by Kaneka Co., Ltd. of 550 micrometer thickness of examples, it applied so that the thickness after drying the polyimide precursor varnish compounded in the synthetic example 5 might be set to 8 micrometers, and it dried for 10 minutes at 80 degrees C first, then, dried for 10 minutes at 120 degrees C, and dried for 15 minutes at 150 more degrees C. Subsequently, heat-treatment was performed to this spreading article at 210 degrees C for 5 minutes, and processing which controls imide-izing and generating capacity was performed.

[0067] Thus, the polyimide precursor of the obtained charge for semiconductor devices of a binder was imide-ized upwards, and 50nm and 100nm of copper spatters were performed for the chromium spatter. The copper layer with a thickness of 1 micrometer was formed in both sides by non-electrolytic copper plating after that, and the metallic foil with resin whose double-sided metal layer is copper was obtained.

[0068] After the metallic foil formation with resin, when the amount of generation of gas was measured, it is 49 ppm and peeling of the metal layer by the generation of gas etc. was not observed. Moreover, it was 16 N/cm when the value when tearing off a metal layer like an example 1 was measured.

[0069] The resist pattern with a thickness of 10 micrometers was produced using the example 2, the same resist, and the mask on the metal deposit of both sides of the obtained metallic foil with resin, electroless nickel plating was given, and it plated to 8 micrometers in thickness. Tinning and gold plate were performed after that and it plated to 5 micrometers which is finally the same height as a resist.

[0070] The resist was removed after plating termination, subsequently software etching was carried out using the ferric chloride water solution, metals other than a wiring part were removed, and the double-sided patchboard was obtained. In the obtained patchboard, thin wiring of 5-micrometer width of face had also pasted up firmly comparatively thick wiring of 100-micrometer width of face with the film, and lack of a circuit pattern etc. was not seen.

[0071] The polyimide precursor varnish compounded in the synthetic example 6 instead of the polyimide precursor varnish compounded in the example 5 of example 6 composition was used, and processing which controls spreading, desiccation, imide-izing, and generating capacity like an example 5 was performed.

[0072] Surface roughening of the side top which imide-ized the polyimide precursor of the obtained charge for semiconductor devices of a binder was carried out by the chromic acid, the neutralization liquid made from SHIPUREI neutralized, the catalyst nucleus was activated with the accelerator made from SHIPUREI, the copper layer with a thickness of 12 micrometers was formed in both sides by non-electrolytic copper plating after that, and the metallic foil with resin whose double-sided metal layer is copper was obtained.

[0073] After the metallic foil formation with resin, when the amount of generation of gas was measured, it is 49 ppm and peeling of the metal layer by the generation of gas etc. was not observed. Moreover, it was 17 N/cm when the value when tearing off a metal layer like an example 1 was measured.

[0074] The resist pattern was produced using the example 1, the same resist, and the mask on the metal layer of both sides of the obtained metallic foil with resin, the double-sided metal was etched like the example 1, the double-sided resist was removed, and the double-sided patchboard was obtained. In the obtained patchboard, both sides had also pasted up firmly comparatively thick wiring of 100-micrometer width of face also for thin wiring of 5-micrometer width of face with the film, and lack of a circuit

pattern etc. was not seen.

[0075]

[Effect of the Invention] There is little generating gas at the time of heat-treatment, and a metal layer and a heat-resistant-resin film paste them up firmly while they can employ the physical properties of a heat-resistant-resin film efficiently, since specific polyimide system adhesives are used for the charge for semiconductor devices of a binder and the metallic foil with resin of this invention. The patchboard using this metallic foil with resin is excellent in generating of lack of a circuit pattern etc. few.

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[Translation done.]

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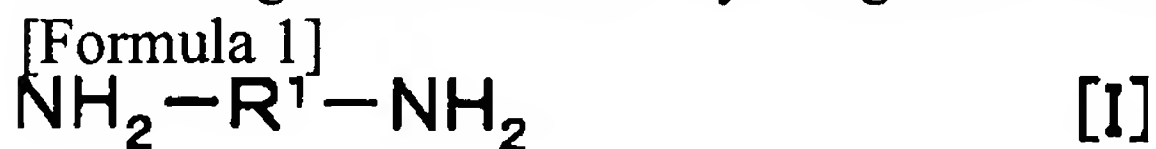
CLAIMS

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[Claim(s)]

[Claim 1] The charge for semiconductor devices of a binder which is a charge of a binder which applied at least to one side of a heat-resistant-resin film the polyimide precursor which uses aromatic series tetracarboxylic dianhydride and diamine as a principal component, and is characterized by diamine containing what is shown by the general formula [I].

[Formula 1]



(R1 expresses the organic radical containing an alkylene group among a formula.)

[Claim 2] The charge for semiconductor devices according to claim 1 of a binder in which a polyimide precursor has a catalyst nucleus.

[Claim 3] The charge for semiconductor devices according to claim 1 of a binder by which the applied polyimide precursor is imide-ized.

[Claim 4] The metallic foil with resin which carried out the laminating of the metal layer on the charge for semiconductor devices according to claim 2 of a binder.

[Claim 5] The patchboard obtained by etching a metal layer at the configuration which suited the circuit pattern by forming a resist layer on the metal layer of a metallic foil with resin according to claim 4, and exposing and developing a resist layer by using as an etching mask the resist which carried out patterning of the resist and carried out patterning, forming a circuit pattern, and removing a resist after circuit pattern formation.

[Claim 6] The patchboard obtained by forming a circuit pattern in the part which removed the resist of the part which forms a resist layer on the metal layer of a metallic foil with resin according to claim 4, and forms a circuit pattern by exposing and developing a resist layer, and removed the resist by plating, exfoliating a resist after that, and removing metal layers other than a circuit pattern.

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(71)出願人 000003159  
東レ株式会社  
東京都中央区日本橋室町2丁目2番1号  
(72)発明者 小國 昌宏  
滋賀県大津市園山1丁目1番1号 東レ株  
式会社滋賀事業場内  
(72)発明者 奥倉 三好  
滋賀県大津市園山1丁目1番1号 東レ株  
式会社滋賀事業場内  
(72)発明者 吉村 利夫  
滋賀県大津市園山1丁目1番1号 東レ株  
式会社滋賀事業場内

最終頁に続く

(54)【発明の名称】 半導体装置用接着材料および樹脂付き金属箔ならびに配線板

(57)【要約】

【課題】耐熱性樹脂フィルムの物性を損なうことがなく、加熱処理時の発生ガスが少なく、耐熱性樹脂フィルムと金属箔とが強固に接着する半導体装置用接着材料、樹脂付き金属箔並びに樹脂付き金属箔を用いた配線板を提供する。

【解決手段】耐熱性樹脂フィルムの少なくとも片面に、芳香族テトラカルボン酸二無水物とジアミンを主成分とするポリイミド前駆体を塗布した接着材料であって、ジアミンが一般式〔I〕で示されるものを含むことを特徴とする半導体装置用接着材料。

【化1】



(式中、R<sup>1</sup>はアルキレン基を含む有機基を示す。)

## 【特許請求の範囲】

【請求項1】耐熱性樹脂フィルム of の少なくとも片面に、芳香族テトラカルボン酸二無水物とジアミンを主成分とするポリイミド前駆体を塗布した接着材料であって、ジアミンが一般式〔I〕で示されるものを含むことを特徴とする半導体装置用接着材料。

## 【化1】



(式中、 $\text{R}^1$ はアルキレン基を含む有機基を表す。)

【請求項2】ポリイミド前駆体が触媒核を有する請求項1記載の半導体装置用接着材料。

【請求項3】塗布されたポリイミド前駆体がイミド化されている請求項1記載の半導体装置用接着材料。

【請求項4】請求項2記載の半導体装置用接着材料の上に金属層を積層した樹脂付き金属箔。

【請求項5】請求項4記載の樹脂付き金属箔の金属層上にレジスト層を形成し、レジスト層を露光・現像することにより配線パターンに合った形状にレジストをパターンニングし、パターンニングしたレジストをエッチングマスクとして金属層をエッチングして配線パターンを形成し、配線パターン形成後にレジストを除去することにより得られる配線板。

【請求項6】請求項4記載の樹脂付き金属箔の金属層上にレジスト層を形成し、レジスト層を露光・現像することにより配線パターンを形成する部分のレジストを除去し、レジストを除去した部分にメッキにより配線パターンを形成し、その後にレジストを剥離し、配線パターン以外の金属層を除去することにより得られる配線板。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明はフレキシブル配線板の製造に用いられる半導体装置用接着材料、樹脂付き金属箔ならびに配線板に関するものである。

## 【0002】

【従来の技術】従来から、耐熱性樹脂フィルムはその樹脂特有の特徴を生かしさまざまな分野で使用されている。例えば、金属箔と接着剤で積層したFPC（フレキシブルプリント基板）、TAB（tape automated bonding）用のフィルムキャリアテープなどは周知の通りである。これらは、ポリイミドなどの耐熱性樹脂フィルムと金属箔をエポキシ樹脂系、アクリル樹脂系、ポリアミド樹脂系、NBR（アクリロニトリル-ブタジエンゴム）系などの接着剤を用いて貼り合わせたものである。このようなFPCやフィルムキャリアテープの諸特性は、現状においては、使用する接着剤の性能に左右されており、耐熱性樹脂フィルムの有する優れた耐熱性やその他の特性が十分に生かされていない。このためポリイミドフィルムを用いても、ポリイミドの耐熱性が350℃以上であるにもかかわらず、FPCやフィルムキャリ

アテープの半田耐熱性は通常300℃以下となってしまう。

【0003】更に、金属箔を貼るのではなく、エポキシ樹脂系、アクリル樹脂系、ポリアミド樹脂系、NBR系などの接着剤の上に金属をスパッタ、あるいは接着剤の上にウェットプロセスにより薄い金属層を形成し、その後メッキによりさらに金属層を形成する方法も知られている。

## 【0004】

10 【発明が解決しようとする課題】このような問題点を解決する方法として、接着剤を用いずに金属箔表面にポリイミド前駆体ないしポリイミドの有機極性溶媒溶液を直接塗布した後、溶媒の乾燥除去、イミド化する方法も知られている。しかしながら、接着剤を用いないため、金属箔とポリイミドとの接着性が不足しており、金属層をバターニングして配線を形成する際に、配線層がポリイミドから剥離してしまう問題があった。

## 【0005】

20 【課題を解決するための手段】すなわち本発明は、耐熱性樹脂フィルム of の少なくとも片面に、芳香族テトラカルボン酸二無水物とジアミンを主成分とするポリイミド前駆体を塗布した接着材料であって、ジアミンが一般式〔I〕で示されるものを含むことを特徴とする半導体装置用接着材料である。

## 【0006】

## 【化2】



30 【0007】（式中、 $\text{R}^1$ はアルキレン基を含む有機基を示す。）

## 【0008】

【発明の実施の形態】本発明の半導体装置用接着材料は、ベースフィルムとなる耐熱性樹脂フィルム上に、予め、接着剤層として芳香族テトラカルボン酸二無水物と柔軟な骨格を有するジアミンを主成分としたポリイミド前駆体を塗布したものであり本発明の樹脂付き金属箔はこの接着材料の上に金属層を形成したものである。

40 【0009】ベースフィルムとなる耐熱性樹脂フィルムとしては、ビスフェノール類のジカルボン酸の縮合物であるポリアリレート、ポリスルホン、またはポリエーテルスルホンに代表されるポリアリルスルホン、ベンゾテトラカルボン酸と芳香族イソシアネートとの縮合物、あるいはビスフェノール類、芳香族ジアミン、ニトロフタル酸の反応から得られる熱硬化性ポリイミド、芳香族ポリイミド、芳香族ポリアミド、芳香族ポリエーテルアミド、ポリフェニレンスルファイド、ポリアリルエーテルケトン、ポリアミドイミド、液晶ポリマーなどの樹脂をフィルムにしたものが挙げられるが、これらに限定されない。具体的な製品としては、東レ・デュポン（株）製「カプトン」、宇部興産（株）製「ユービレックス」、

鐘淵化学工業(株)製「アピカル」、東レ(株)製「ミクトロン」、(株)クラレ製「ベキトラ」などが挙げられる。

【0010】これらの樹脂 これらの樹脂の中では芳香族ポリイミド、芳香族ポリアミド、特にピロメリット酸二無水物、あるいはビフェニルテトラカルボン酸二無水物とジアミノジフェニルエーテル、パラフェニレンジアミンなどの芳香族ジアミンとの縮合物である芳香族ポリイミドが好ましい。

【0011】上記耐熱性 上記耐熱性樹脂フィルム表面にコロナ放電処理や低温プラズマ処理、あるいは公知のウェットプロセス処理などを施すのは任意であり、とりわけ適当なプラズマ処理を施すことが接着力向上の点で好ましい。

【0012】耐熱性樹脂フィルムの厚みとしては、好ましくは5~125 $\mu$ m、より好ましくは20~80 $\mu$ mである。薄すぎるとフィルムの搬送性に支障をきたすので上記範囲が好ましい。

【0013】上記耐熱性樹脂フィルムの少なくとも片面に塗布されるポリイミド前駆体は、ベースフィルムである耐熱性樹脂フィルムと金属層とを接着させる接着剤として機能する。このようなポリイミド前駆体は芳香族テトラカルボン酸二無水物と柔軟な骨格を有するジアミンとを主成分とするものである。

【0014】芳香族テトラカルボン酸二無水物の具体例としては、ピロメリット酸二無水物、3,3',4,4'-ビフェニルテトラカルボン酸二無水物、2,3,3',4'-ビフェニルテトラカルボン酸二無水物、3,3',4,4'-ベンゾフェノンテトラカルボン酸二無水物、2,2',3,3'-ベンゾフェノンテトラカルボン酸二無水物、2,2',3,3'-ビフェニルテトラカルボン酸二無水物、2,2'-ビス(3,4-ジカルボキシフェニル)プロパン二無水物、2,2'-ビス(2,3-ジカルボキシフェニル)プロパン二無水物、ビス(3,4-ジカルボキシフェニル)エーテル二無水物、ビス(3,4-ジカルボキシフェニル)スルホン二無水物、1,1'-ビス(2,3-ジカルボキシフェニル)エタン二無水物、ビス(2,3-ジカルボキシフェニル)メタン二無水物、2,3,6,7-ナフタレンテトラカルボン酸二無水物、1,4,5,8-ナフタレンテトラカルボン酸二無水物、1,2,5,6-ナフタレンテトラカルボン酸、1,2,3,4-ベンゼンテトラカルボン酸二無水物、3,4,9,10-ペリレンテトラカルボン酸二無水物、2,3,6,7-アントラセンテトラカルボン酸二無水物、1,2,7,8-フェナントレンテトラカルボン酸二無水物などが挙げられる。これらの酸二無水物は1種あるいは2種類以上混合して用いられる。

【0015】本発明で好ましく用いられるジアミンとしては、一般式[I]で表されるものが好ましく挙げられ

る。

【0016】

【化3】



[I]

【0017】式中、R<sup>1</sup>はアルキレン基を含む有機基を示す。アルキレン基としては、メチレン基、エチレン基、プロピレン基、ブチレン基、ヘキシレン基、オクチレン基、ポリメチレン基などが挙げられ、これらは適当な置換基を有していてもよく、鎖中にエーテル結合やエステル結合、アミノ結合、アミド結合、ウレタン結合、ウレア結合、カーボネート結合などを鎖中に含んでもよい。この場合の置換基としてはアルキル基、フェニル基、メトキシ基、フェノキシ基、ニトロ基、水酸基、アミノ基、フッ素原子、塩素原子などが挙げられるが、これらに限定されない。このような柔軟な骨格を有するジアミンは単独あるいは2種以上混合して用いられるが、接着性や耐熱性などの要求特性を満足させる目的から2種以上混合して用いることが好ましい。

【0018】また、必要に応じて一般式[I]で示される以外のジアミンを混合することも接着剤としての機能とポリイミドの耐熱性の両方を引き出す点から好ましい。このようなジアミンとしては特に限定されないが、4,4'-ジアミノジフェニルエーテル、4,4'-ジアミノジフェニルメタン、4,4'-ジアミノジフェニルスルホン、パラフェニレンジアミン、1,1,3,3-テトラメチル-1,3-ビス(4-アミノフェニル)ジシロキサン、1,1,3,3-テトラフェノキシ-1,3-ビス(2-アミノエチル)ジシロキサン、1,1,3,3,5,5-ヘキサメチル-1,5-ビス(4-アミノフェニル)トリシロキサン、1,1,3,3-テトラフェニル-1,3-ビス(2-アミノエチル)ジシロキサン、1,1,3,3-テトラフェニル-1,3-ビス(3-アミノプロピル)ジシロキサン、1,1,5,5-テトラフェニル-3,3-ジメチル-1,5-ビス(3-アミノプロピル)トリシロキサン、1,1,5,5-テトラフェニル-3,3-ジメトキシ-1,5-ビス(4-アミノプロピル)トリシロキサン、1,1,5,5-テトラフェニル-3,3-ジメトキシ-1,5-ビス(5-アミノペンチル)トリシロキサン、1,1,3,3-テトラメチル-1,3-ビス(2-アミノエチル)ジシロキサン、1,1,3,3-テトラメチル-1,3-ビス(3-アミノプロピル)ジシロキサン、1,1,3,3-テトラメチル-1,3-ビス(4-アミノブチル)ジシロキサン、1,3-ジメチル-1,3-ジメトキシ-1,3-ビス(4-アミノブチル)ジシロキサン、1,1,5,5-テトラメチル-3,3-ジメトキシ-1,5-ビス(2-アミノエチル)トリシロキサン、1,1,5,5-テトラメチル-3,3-ジメトキシ-1,5-ビス(4-アミノブチ



ル)トリシロキサン、1, 1, 5, 5-テトラメチルー3, 3-ジメトキシ-1, 5-ビス(5-アミノペンチル)トリシロキサン、1, 1, 3, 3, 5, 5-ヘキサメチルー1, 5-ビス(3-アミノプロピル)トリシロキサン、1, 1, 3, 3, 5, 5-ヘキサプロピルー1, 5-ビス(3-アミノプロピル)トリシロキサンなどが挙げられるが、これらに限定されず、鎖中にエーテル結合やエステル結合、アミノ結合、アミド結合、ウレタン結合、ウレア結合、カーボネート結合などを含んでもよい。これらのジアミンは単独または2種以上混合して用いることができる。

【0019】本発明のポリイミド前駆体において、全ジアミン化合物に対して一般式〔I〕に該当するジアミンの割合はイミド化後のカール防止効果及び接着性の向上効果の点からは50mol%以上であることが好ましい。

【0020】上記芳香族テトラカルボン酸二無水物とジアミンとの反応は、略化学量論量の芳香族テトラカルボン酸またはその無水物とジアミンとをN, N-ジメチルホルムアミド、N, N-ジメチルアセトアミド、N-メチルー2-ピロリドン等の有機溶媒中で0~80℃で反応させればよい。これらの有機溶媒は単独あるいは二種以上混合して用いられ、ポリイミド前駆体が析出しない程度であればベンゼン、トルエン、ヘキサン、シクロヘキサン、テトラヒドロフラン、メチルエチルケトン等の溶媒を加えてもよい。ポリイミド前駆体ワニス濃度は特に限定されないが、5~60重量%が好ましく、10~40重量%が特に好ましい。

【0021】本発明の半導体装置用接着材料及び樹脂付き金属箔においては、耐熱性樹脂フィルム上にポリイミド前駆体を塗布している。ポリイミド前駆体のイミド化に関しては、ポリイミドとしての性能を引き出すために金属層形成前に行なわれていることが好ましく、特に、ポリイミド前駆体を耐熱性樹脂フィルムに塗布した直後に行なわれていることが好ましい。本発明において使用されるポリイミド前駆体はイミド化した後は熱可塑性であるので、ポリイミドの状態では接着剤として使用できる利点を有している。熱硬化性のポリイミドの場合、硬化すなわちイミド化の際に水が発生するため、この水がガスとなり発泡が生じてしまう。

【0022】本発明においてイミド化した後のポリイミド前駆体は、加熱処理時の発生ガスが少ないので、水その他のガスによる発泡が少なくなるが、イミド化した後の加熱温度100~300℃において発生するガス量が250ppm以下であることが好ましい。より好ましくは150ppm以下、更に好ましくは100ppm以下である。ここで加熱温度100~300℃において発生するガス量とは、熱重量分析・微分解重量分析・質量分析法により測定して求めたものである。

【0023】次に、上記した本発明の半導体装置用接着

材料の製造方法を説明する。

【0024】まず、耐熱性樹脂フィルム上に上記ポリイミド前駆体ワニスを含む溶媒溶液を製膜用スリットから吐出させて均一に塗布する。塗布方法としては、ロールコーター、ナイフコーター、密封コーター、コンマコーター、ドクターブレードフロートコーターなどによるものが挙げられる。次に上記のように耐熱性樹脂フィルムに塗布した溶液の溶媒を、60~190℃程度の温度で連続的または断続的に1~60分間で加熱除去した後、更にイミド化及びガス発生量を250ppm以下となすための加熱処理を行う。イミド化及びガス発生量を250ppm以下となすための加熱処理としては、200~350℃の範囲で1~15分程度の加熱処理を行うことが好ましい。このようにしてポリイミド前駆体をイミド化しポリイミド膜を形成し、半導体装置用接着材料を得る。

【0025】また、本発明においてポリイミド前駆体のイミド化後の弾性率が耐熱性樹脂フィルムの弾性率よりも小さくなることが好ましい。

【0026】ポリイミド前駆体をイミド化した後の厚みとしては、好ましくは0.05~50μm、より好ましくは0.1~25μmである。薄すぎると接着効果が弱くなる。

【0027】本発明において、ポリイミド前駆体中には触媒核を有することも好ましい。ここで言う触媒核とは、そのままではメッキ成長の核として働かないが、活性化処理をすることでメッキ成長の核として働くものである。触媒核の添加は通常ポリイミド前駆体ワニスの状態に添加されるが、場合によっては耐熱性樹脂フィルム塗布後に添加してもよく、ポリイミド前駆体をイミド化した後に添加してもよい。触媒核は、金属層をメッキで形成する際のコアとなるものであり、パラジウムやニッケル、クロムなどが好ましく、さらにパラジウムが好ましい。上記ポリイミド前駆体中に含まれる触媒核の含有割合は、好ましくはポリイミド前駆体100重量部に対して0.001~100重量部である。

【0028】次に、樹脂付き金属箔の場合はポリイミド前駆体または前駆体をイミド化した膜の上に金属層を形成する。金属層形成方法としては、金属箔を貼り付ける方法、スパッタや蒸着による方法、メッキによる方法などが挙げられる。金属層を構成する金属としては、銅、ニッケル、クロム、スズ、亜鉛、鉛、金、ロジウム、パラジウムなどが挙げられるが、これらに限定されない。これらの金属は単独で用いても複数組み合わせ用いてもよい。

【0029】金属箔を貼り合わせる場合、70~350℃でラミネート、あるいは比較的低温の40~200℃でラミネートした後に高温の100~350℃で処理することにより金属箔を接着させることが好ましい。

【0030】スパッタや蒸着の場合、適当な厚み、例え



ば0.0001~10 $\mu$ mの厚みになるように接着剤上に金属層を形成する。

【0031】メッキの場合、直接メッキを施すのではなく、メッキ前に核となる金属薄膜をポリイミド前駆体または前駆体をイミド化した膜の上に形成し、しかる後にメッキを施すのが一般的である。このような核となる金属薄膜を形成する方法としては、ウェットプロセスとドライプロセスとに分けられる。ウェットプロセスの場合、更にポリイミド前駆体または前駆体をイミド化した膜が触媒核を有している場合と有していない場合とで分けられる。触媒核を有していない場合、まずパラジウムやニッケル、クロムなどの触媒付与の処理を行い、必要であれば付与した触媒を活性化する。触媒核を有している場合は必要であれば触媒を活性化する。ドライプロセスの場合、ポリイミド前駆体あるいは前駆体をイミド化した膜にクロムやニッケル、銅などの金属をスパッタするが、銅などの金属を単独でスパッタしてもよく、クロム-銅やニッケル-銅などを組み合わせてスパッタしてもよい。核となる金属薄膜の厚みについては特に規定されないが、好ましくは1~1000nmである。厚すぎると金属薄膜形成に時間がかかり、薄すぎると欠点が生じて後述するメッキに障害となる。このようにして形成した金属薄膜上にメッキにより金属層を形成する。金属層は無電解メッキのみで形成してもよいが、無電解メッキと電解メッキを併用して形成してもよく、電解メッキのみで形成してもよい。無電解メッキとして例えば銅をメッキする場合は硫酸銅とホルムアルデヒドの組み合わせなどが用いられる。また電解メッキとして例えば銅をメッキする場合、通常硫酸銅メッキ液、シアン化銅メッキ液、ピロリン酸銅メッキ液などが用いられる。

【0032】金属層厚みは樹脂付き金属箔をどのように加工するかによっても左右される。すなわち、樹脂付き金属箔を用いてアディティブ方式（セミアディティブ方式あるいはフルアディティブ方式）にて配線板を形成する場合、金属層の上に更にメッキにて金属を積層するので、樹脂付き金属箔の金属層厚みは0.1~10 $\mu$ mの範囲が好ましい。逆に樹脂付き金属箔を用いてサブトラクティブ方式にて配線板を形成する場合、金属箔をそのまま配線として使用するので、樹脂付き金属箔の金属層厚みは3~40 $\mu$ mの範囲が好ましい。

【0033】上記金属層を形成する一連の行程としては、例えば以下のような手順が挙げられる。すなわち、まず耐熱性樹脂フィルムに塗布したポリイミド前駆体あるいは前駆体をイミド化した半導体装置用接着材料の接着剤面の整面、表面洗浄を行う。次にソフトエッチングを実施し、硫酸により酸洗浄を行い、塩酸による前処理を施す。触媒核が含有されている場合は引き続いて触媒活性化処理を行い、触媒核が含有されていない場合には触媒付与を行った後に触媒活性化処理を行う。しかる後に無電解金属メッキを施し、必要であれば無電解メッキ

後に電解金属メッキを行い、金属層を形成する。

【0034】本発明においては、ベースフィルムとなる耐熱性樹脂フィルム上に接着剤となりうるポリイミド前駆体または前駆体をイミド化した膜を形成することで半導体装置用接着材料を作製し、その上に金属層を形成して樹脂付き金属箔を得ている。ポリイミド前駆体をイミド化することにより、耐熱性樹脂フィルム上に直接金属層を形成するよりも強固な接着力が得られ、とりわけ金属層を所定の配線パターンにエッチングした際にも良好な接着力を得ることができる。

【0035】本発明において接着力とは、JIS C5016 7.1項に準じ、導体幅3mmのパターンを使用し、金属箔を180度の方向に50mm/分の速度で引き剥がした時の値を意味し、通常5N/cm以上が好ましく、より好ましくは10N/cm以上とされているが、本発明の樹脂付き金属箔によれば、容易に10N/cm以上の値を得ることが可能となる。また、耐熱性樹脂フィルムが本来有する特性を損なわない利点も有している。

【0036】上記本発明の樹脂付き金属箔は、金属層上にレジスト層を形成し、レジスト層を露光・現像することにより配線パターンに合った形状にレジストをパターンニングし、パターンニングしたレジストをエッチングマスクとして金属層をエッチングして配線パターンを形成し、配線パターン形成後にレジストを除去することにより得られる配線板として好ましく使用される。

【0037】また、上記本発明の樹脂付き金属箔は、金属層上にレジスト層を形成し、レジスト層を露光・現像することにより配線パターンを形成する部分のレジストを除去し、レジストを除去した部分にメッキにより配線パターンを形成し、その後にレジストを剥離し、配線パターン以外の金属層を除去することにより得られる配線板とすることも好ましい。

【0038】本発明の樹脂付き金属箔は、耐熱性樹脂フィルムの片面あるいは両面に金属層を有しており、セミアディティブ方式あるいはサブトラクティブ方式を用いて配線を形成することにより片面あるいは両面配線板を形成することができ、フレキシブル配線板用途に好ましく使用できる。

【0039】

【実施例】以下実施例を挙げて本発明を説明するが、本発明はこれらの例によって限定されるものではない。

【0040】合成例1

温度計、攪拌装置、還流器を備えた500mlのフラスコ内に窒素雰囲気下に置換し、N,N-ジメチルアセトアミド128.8gを入れ、下記に示されたジアミン10.4g(0.1mol)と3,3',4,4'-ベンゾフェノンテトラカルボン酸二無水物32.2g(0.1mol)を加え、窒素雰囲気下で10℃で1時間、引き続いて50℃で3時間攪拌しながら反応させ、ポリイ

ミド前駆体ワニスを得た。

【0041】

【化4】



【0042】合成例2

合成例1で得たポリイミド前駆体ワニスにパラジウム触媒核を5g添加し、触媒核含有ポリイミド前駆体ワニスを得た。

【0043】合成例3

合成例1と同じ反応容器を用い、N, N-ジメチルアセトアミド166.8gを入れ、下記に示されたジアミン7.4g(0.05mol)、エチレンジアミン0.6g(0.01mol)、パラフェニレンジアミン4.3g(0.04mol)、3, 3', 4, 4'-ビフェニルテトラカルボン酸二無水物29.4g(0.10mol)を加え、窒素雰囲気下で10℃で1時間、引き続いて50℃で3時間攪拌しながら反応させ、ポリイミド前駆体ワニスを得た。

【0044】

【化5】



【0045】合成例4

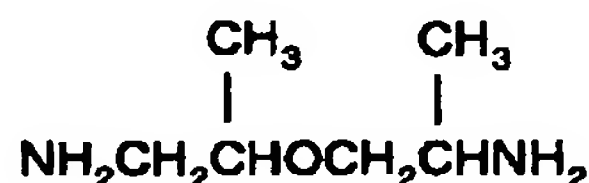
合成例2で得たポリイミド前駆体ワニスにパラジウム触媒核を3g添加し、触媒核含有ポリイミド前駆体ワニスを得た。

【0046】合成例5

合成例1と同じ反応容器を用い、N, N-ジメチルアセトアミド191.2gを入れ、下記に示されたジアミン6.6g(0.05mol)、ヘキサメチレンジアミン1.2g(0.01mol)、1, 1, 3, 3-テトラメチル-1, 3-ビス(アミノメチル)ジシロキサン1.9g(0.01mol)、4, 4'-ジアミノジフェニルメタン5.9g(0.03mol)、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物32.2g(0.1mol)を加え、窒素雰囲気下で10℃で1時間、引き続いて50℃で3時間攪拌しながら反応させ、ポリイミド前駆体ワニスを得た。

【0047】

【化6】



【0048】合成例6

合成例5で得たポリイミド前駆体ワニスにパラジウム触媒核を10g添加し、触媒核含有ポリイミド前駆体ワニスを得た。

【0049】合成例7

合成例1と同じ反応容器を用い、N, N-ジメチルアセ

トアミド172gを入れ、パラフェニレンジアミン10.8gを溶解し、3, 3', 4, 4'-ベンゾフェノンテトラカルボン酸二無水物32.2gを加え、窒素雰囲気下で10℃で1時間、引き続いて50℃で3時間攪拌しながら反応させ、シロキサン系ジアミンを含まないポリイミド前駆体ワニスを得た。

【0050】実施例1

50μm厚の宇部興産(株)製ポリイミドフィルム「ユービレックスS」の片面上に合成例1で合成したポリイミド前駆体ワニスを乾燥後の膜厚が12μmになるように塗布し、まず80℃で10分間乾燥し、次に130℃で10分間乾燥し、更に150℃で15分間乾燥した。ついで、イミド化および発生ガス量を制御する処理として、250℃で5分加熱を施した。

【0051】次に得られた接着材料のポリイミド前駆体をイミド化した側をイソプロパノールで脱脂し、水酸化ナトリウム含有溶液にてソフトエッチングし、塩酸で中和し、奥野製薬工業(株)製OPC-50インデューサーにて触媒付与し、奥野製薬工業(株)製OPC-150クリスターにて還元処理を施し、その後に無電解銅メッキで厚さ0.5μmまでメッキし、電解銅メッキにより最終的に厚さ35μmの銅層を形成し、金属層が銅である片面樹脂付き金属箔を得た。

【0052】樹脂付き金属箔形成後、250℃1時間加熱処理してガス発生量を測定したところ、42ppmであり、ガス発生による金属層の剥がれなどは観察されなかった。また、形成した樹脂付き金属箔における金属層と基材フィルムとの接着力を調べるため、JIS C5016 7.1項に準じ、導体幅3mmのパターンを使用し、金属層を180度の方向に50mm/分の速度で引き剥がした時の値を測定したところ、12N/cmであった。

【0053】得られた片面の樹脂付き金属箔の金属層の上にフォトレジストを乾燥膜厚が5μmになるように塗布・乾燥し、線幅が5~100μmであるような配線パターンに合ったマスクを用いて露光・現像を施し、配線層パターン部分のみが残ったレジストパターンを得た。次に、レジストが除去された部分の金属を10%塩化鉄水溶液にてエッチングし、片面配線板を得た。得られた配線板では、5μm幅の細い配線も100μm幅の比較的太い配線もフィルムと強固に接着しており、配線パターンの欠落などは見られなかった。

【0054】比較例1

実施例1において、合成例1で合成したポリイミド前駆体ワニスの代わりに合成例7で合成したワニスを用いた以外は実施例1と同様にして樹脂付き金属箔を作製した。ガス発生量は1350ppmであり、多数箇所では金属層の剥がれが生じた。実施例1と同様にして金属層と基材フィルムとの接着力を測定したところ、1N/cm以下であり、簡単に金属層と基材フィルムとが剥離し、



実用レベルではなかった。

#### 【0055】実施例2

合成例1で合成したポリイミド前駆体ワニスの代わりに合成例2で合成したポリイミド前駆体ワニスを使用し、実施例1と同様にして塗布、乾燥、イミド化および発生ガス量を制御する処理を行った。

【0056】得られた半導体装置用接着材料のポリイミド前駆体ワニスをイミド化した側をイソプロパノールで脱脂し、水酸化ナトリウム含有溶液にてソフトエッチングし、塩酸で中和し、奥野製薬工業(株)製OPC-150クリスターにて還元処理を施し、奥野製薬工業(株)製TMP化学ニッケルHR-Tにて無電解ニッケルメッキを施し、その後に無電解銅メッキで厚さ1 $\mu$ mまでメッキし、電解銅メッキにより最終的に厚さ3 $\mu$ mの銅層を形成し、金属層が銅である片面樹脂付き金属箔を得た。

【0057】樹脂付き金属箔形成後、ガス発生量を測定したところ、42ppmであり、ガス発生による金属層の剥がれなどは観察されなかった。また、形成した樹脂付き金属箔における金属層と基材フィルムとの接着力を調べるため、実施例1と同様にして引き剥がした時の値を測定したところ、13N/cmであった。

【0058】得られた片面の樹脂付き金属箔の金属層の上にフォトリソを乾燥膜厚が5 $\mu$ mになるように塗布・乾燥し、線幅が5~100 $\mu$ mであるような配線パターンに合ったマスクを用いて露光・現像を施し、配線層パターン部分のみが除去されたレジストパターンを得た。次に、レジストが除去された部分の金属に無電解銅メッキと電解銅メッキを施し、4.5 $\mu$ mまでメッキした。その後にスズメッキと金メッキを施し、最終的にレジストと同じ高さである5 $\mu$ mまでメッキを施した。メッキ終了後、レジストを除去し、次いで塩化鉄水溶液を用いてソフトエッチングして配線部分以外の金属を除去し、片面配線板を得た。得られた配線板では、5 $\mu$ m幅の細い配線も100 $\mu$ m幅の比較的太い配線もフィルムと強固に接着しており、配線パターンの欠落などは見られなかった。

#### 【0059】実施例3

50 $\mu$ m厚の東レ・デュポン(株)製ポリイミドフィルム「カプトンEN」の両面上にまずプラズマ処理を施し、合成例3で合成したポリイミド前駆体ワニスを乾燥後の膜厚が18 $\mu$ mになるように塗布し、まず80℃で10分間乾燥し、次に120℃で10分間乾燥し、更に150℃で15分間乾燥した。ついで該塗布品に210℃で5分加熱処理を施して、イミド化および発生ガス量を制御する処理を行った。

【0060】このようにして得られた半導体装置用接着材料のポリイミド前駆体をイミド化した上に荏原ユー

ジライト(株)製DP-300と塩酸とを用いてプレディップし、荏原ユージライト(株)製DP-300とDP-350と塩酸とを用いて触媒付与し、荏原ユージライト(株)製DP-400A~DとDP-410とを用いて触媒を活性化し、荏原ユージライト(株)製DP-500を用いて触媒の還元処理を施し、荏原ユージライト(株)製PB-242Dにて酸性脱脂を施し、硫酸にて酸洗浄し、その後に硫酸銅を用いて電解銅メッキを施し、厚さ8 $\mu$ mの銅層を両面に形成し、両面の金属層が銅である樹脂付き金属箔を得た。

【0061】樹脂付き金属箔形成後、ガス発生量を測定したところ、45ppmであり、ガス発生による金属層の剥がれなどは観察されなかった。また、実施例1と同様にして金属層を引き剥がした時の値を測定したところ、14N/cmであった。

【0062】得られた樹脂付き金属箔の両面の金属層の上に実施例1と同様のレジストとマスクを用いてレジストパターンを作製し、実施例1と同様にして両面の金属をエッチングし、両面のレジストを除去して両面配線板を得た。得られた配線板では、両面共に5 $\mu$ m幅の細い配線も100 $\mu$ m幅の比較的太い配線もフィルムと強固に接着しており、配線パターンの欠落などは見られなかった。

#### 【0063】実施例4

合成例3で合成したポリイミド前駆体ワニスの代わりに合成例4で合成したポリイミド前駆体ワニスを使用し、プレディップ工程までは実施例3と同様にした。次に荏原ユージライト(株)製DP-400A~DとDP-410とを用いて触媒を活性化し、荏原ユージライト(株)製DP-500を用いて触媒の還元処理を施し、荏原ユージライト(株)製PB-242Dにて酸性脱脂を施し、硫酸にて酸洗浄し、その後に硫酸銅を用いて電解銅メッキを施し、厚さ2 $\mu$ mの銅層を両面に形成し、両面の金属層が銅である樹脂付き金属箔を得た。

【0064】樹脂付き金属箔形成後、ガス発生量を測定したところ、45ppmであり、ガス発生による金属層の剥がれなどは観察されなかった。また、実施例1と同様にして金属層を引き剥がした時の値を測定したところ、15N/cmであった。

【0065】得られた樹脂付き金属箔の両面の金属層の上に実施例2と同様のレジストとマスクを用いて厚さ15 $\mu$ mのレジストパターンを作製し、電解銅メッキを施してレジストと同じ高さである厚さ15 $\mu$ mまでメッキした。その後にレジストを除去し、次いで全体を塩化銅水溶液を用いてソフトエッチングし、配線部分以外の金属を除去することで両面配線板を得た。得られた配線板では、5 $\mu$ m幅の細い配線も100 $\mu$ m幅の比較的太い配線もフィルムと強固に接着しており、配線パターンの欠落などは見られなかった。

## 【0066】実施例5

50 $\mu$ m厚の鐘淵化学工業(株)製ポリイミドフィルム「アピカルNP I」の両面上にまずプラズマ処理を施し、合成例5で合成したポリイミド前駆体ワニスを乾燥後の膜厚が8 $\mu$ mになるように塗布し、まず80℃で10分間乾燥し、次に120℃で10分間乾燥し、更に150℃で15分間乾燥した。ついで該塗布品に210℃で5分加熱処理を施して、イミド化および発生ガス量を制御する処理を行った。

【0067】このようにして得られた半導体装置用接着材料のポリイミド前駆体をイミド化した上にクロムスパッタを50nm、銅スパッタを100nm施した。その後、無電解銅メッキにて厚さ1 $\mu$ mの銅層を両面に形成し、両面の金属層が銅である樹脂付き金属箔を得た。

【0068】樹脂付き金属箔形成後、ガス発生量を測定したところ、49ppmであり、ガス発生による金属層の剥がれなどは観察されなかった。また、実施例1と同様にして金属層を引き剥がした時の値を測定したところ、16N/cmであった。

【0069】得られた樹脂付き金属箔の両面の金属メッキ層の上に実施例2と同様のレジストとマスクを用いて厚さ10 $\mu$ mのレジストパターンを作製し、無電解ニッケルメッキを施して厚さ8 $\mu$ mまでメッキした。その後、スズメッキと金メッキを施し、最終的にレジストと同じ高さである5 $\mu$ mまでメッキを施した。

【0070】メッキ終了後、レジストを除去し、次いで塩化鉄水溶液を用いてソフトエッチングして配線部分以外の金属を除去し、両面配線板を得た。得られた配線板では、5 $\mu$ m幅の細い配線も100 $\mu$ m幅の比較的太い配線もフィルムと強固に接着しており、配線パターンの欠落などは見られなかった。

## 【0071】実施例6

合成例5で合成したポリイミド前駆体ワニスの代わりに合成例6で合成したポリイミド前駆体ワニスを使用し、実施例5と同様にして塗布、乾燥、イミド化および発生ガス量を制御する処理を行った。

【0072】得られた半導体装置用接着材料のポリイミド前駆体をイミド化した側の上をクロム酸により表面粗化し、シブレイ(株)製中和液にて中和し、シブレイ(株)製アクセラレーターにて触媒核の活性化を行い、その後、無電解銅メッキにて厚さ12 $\mu$ mの銅層を両面に形成し、両面の金属層が銅である樹脂付き金属箔を得た。

【0073】樹脂付き金属箔形成後、ガス発生量を測定したところ、49ppmであり、ガス発生による金属層の剥がれなどは観察されなかった。また、実施例1と同様にして金属層を引き剥がした時の値を測定したところ、17N/cmであった。

【0074】得られた樹脂付き金属箔の両面の金属層の上に実施例1と同様のレジストとマスクを用いてレジストパターンを作製し、実施例1と同様にして両面の金属をエッチングし、両面のレジストを除去して両面配線板を得た。得られた配線板では、両面共に5 $\mu$ m幅の細い配線も100 $\mu$ m幅の比較的太い配線もフィルムと強固に接着しており、配線パターンの欠落などは見られなかった。

## 【0075】

【発明の効果】本発明の半導体装置用接着材料及び樹脂付き金属箔は、特定のポリイミド系接着剤を用いるため、耐熱性樹脂フィルムの物性を生かせると共に、加熱処理時の発生ガスが少なく、かつ金属層と耐熱性樹脂フィルムとが強固に接着したものである。該樹脂付き金属箔を用いた配線板は配線パターンの欠落などの発生が少なく優れたものである。

フロントページの続き

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